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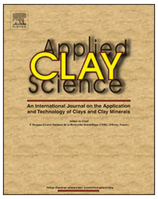

Research Paper

# Adsorption of vanadium (V) on natural kaolinite and montmorillonite: Characteristics and mechanism

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ABSTRACT

Knowledge on adsorption behaviour of vanadium (V) on natural clay minerals is critical to understand V mobility in soil and aqueous systems. In this study, the characteristics and mechanisms of V(V) adsorption on two abundant soil clay minerals, namely, natural kaolinite and montmorillonite, as well as the effects of solution pH and ionic strength on the adsorption process were investigated. The results showed that the kinetics of V(V) adsorption on kaolinite and montmorillonite conformed to pseudo second-order, and reached equilibrium within 240 min and 360 min respectively. The adsorption isotherms of V(V) on kaolinite were better fit with the Freundlich model, while the Langmuir model was a better fit for montmorillonite. The Langmuir model indicated that natural montmorillonite and kaolinite have low affinity for V(V) anions with maximum adsorption capacity of 0.98 $mg \cdot g^{-1}$ and 0.78 $mg \cdot g^{-1}$, respectively. The higher capacity was found at pH 4–10 due to the mass formation of deprotonated hydroxyl groups for V adsorption. The V adsorption capacity on montmorillonite increased with the increasing ionic strength of $NaNO_3$. The results of pH and ionic-strength effect showed that surface complexation and electrostatic interaction may be the V(V) adsorption mechanisms.

## 1. Introduction

Vanadium (V) is a transition metal that widely exists in earth's crust with a global average concentration of 150 $mg \cdot kg^{-1}$ (Byerrum et al., 1974). Anthropogenic activities have caused severe environmental V pollution in recent years, especially when V is commonly used in steel, metallurgy, ceramics, batteries and other activities (Imtiaz et al., 2015). It has been reported that approximately 30–40% of V from the refining industry was discharged into the environment, enriching V in soil and water (Hope, 1997). For example, the content of V in soils from a stone coal smelting area reached up to 1538 $mg \cdot kg^{-1}$ and 3600 $mg \cdot kg^{-1}$ in a mining district (Panichev et al., 2006; Xiao et al., 2015). Although V is an essential element for living creatures and thereby less toxic than other heavy metals (Pyrzyńska and Wierzbicki, 2004), its adverse effects have been revealed. It is reported that high V content inhibited microbial activities and plant growth and degraded water quality (Panichev et al., 2006; Venkataraman and Sudha, 2005; Xiao et al., 2017a; Xiao et al., 2017b). Some studies also showed prolonged exposure to a high level of V damaged the respiratory system and increased the risk of lung cancer (Léonard and Gerber, 1994; Mukherjee et al., 2004). As such, vanadium has been recognized as a potentially dangerous pollutant in the same class as mercury, lead and arsenic and has been listed on the United States Environment Protection Agency candidate contaminant list (Lazaridis et al., 2003; USEPA, 2005; Padilla-Rodríguez et al., 2015). Moreover, V(V) is the most toxic and migratable species, more attention should be paid to its mobility in soil and aqueous systems (Pyrzyńska and Wierzbicki, 2004).

When V enters soil and water, it interacts with minerals and tends to accumulate as V is absorbed to iron and aluminium hydrous oxides, as well as clay minerals. Clay minerals play an important role in soils and sediments acting as a natural scavenger of pollutants by taking up cations and anions through either ion exchange or adsorption or both (Bhattacharyya and Gupta, 2008). To date, many studies of adsorption on natural clay minerals have focused on heavy metals such as Cd(II), Cu(II), Pb(II), Cr(III/VI) and As(III/V) (Bhattacharyya and Gupta, 2006; Dos Anjos et al., 2014; Jiang et al., 2010; Ren et al., 2014; Uddin, 2017). There is some information about the adsorption of V(V) on soils, soil colloids and goethite. For instance, soil type and pH affected the adsorption capacity of V(V) on soils (Gäbler et al., 2009; Larsson et al., 2017). Vanadium adsorption on natural soil colloids were pH-dependent with high capacity of 41.5–286 $mg \cdot g^{-1}$ (Luo et al., 2017). The adsorption of V(V) on goethite mainly occurred by the formation of inner-sphere complexes of $Fe_2O_2V(OH)_2^+$ and $Fe_2O_2VO(OH)$ (Peacock and Sherman, 2004). Dos Anjos et al. (2014) have reported that V(V) in a multi-element solution was less retained onto montmorillonite in trace concentrations (0.05 $mg \cdot L^{-1}$). However, relatively little is known

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**Table 1**
Chemical composition and BET area surface of kaolinite and montmorillonite.

| Clay minerals | Chemical composition (wt., %) | | | | | | | | BET surface area ($m^2 \cdot g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | MgO | $Na_2O$ | CaO | $Fe_2O_3$ | $K_2O$ | $TiO_2$ | |
| Kaolinite | 53.70 | 44.97 | 0.15 | 0.13 | 0.30 | 0.25 | 0.04 | 0.20 | 14.15 |
| Montmorillonite | 61.02 | 18.54 | 5.70 | 3.00 | 2.60 | 1.69 | 0.77 | 0.11 | 107.4 |

Note: Chemical compositions of the clay minerals were obtained from the provider company.

about V(V) adsorption on natural clay minerals.

Kaolinite and montmorillonite are the most abundant minerals in soils and sediments, and they are typical clay minerals of 1:1 (one tetrahedral and one octahedral sheet in each layer) and 2:1 (two tetrahedral and one octahedral sheet) layer types, respectively. In this work, batch experiments were conducted to 1) study the adsorption kinetics and equilibrium isotherms characteristics of V(V) adsorption on natural kaolinite and montmorillonite, 2) discuss the effects of initial solution pH and ionic strength on the V(V) adsorption process, and 3) elucidate the possible adsorption mechanism.

## 2. Materials and methods

### 2.1. Materials

Kaolinite and montmorillonite were obtained from Aladdin Chemical Reagent Co., Ltd., and Zhejiang Sanding Technology Corporation Co., Ltd., respectively. Chemical composition and BET surface area of the clay minerals are shown in Table 1. Kaolinite and montmorillonite were refluxed with 2 $mol \cdot L^{-1}$ $HNO_3$ for 4 h at 60 °C to remove metallic impurities and then repeatedly washed with ultrapure (Milli-Q) water until a supernatant with pH 6 was attained (Sun et al., 2017). The solid was dried at 105 °C in an oven and smashed to $<$ 0.15 mm for adsorption experiment. All chemical agents including $NaNO_3$, $NaVO_3$, $HNO_3$ and NaOH were analytical reagent grade.

### 2.2. Adsorption experiment

The adsorption experiments were completed in 100-mL polyethylene centrifuge tubes, which contained 50 mL of adsorption solution and 0.2 g of dry clay mineral. The centrifuge tubes were oscillated on shaker at 250 rpm and 25 ± 1 °C. Adsorption solution was prepared by dissolving sodium metavanadate ($NaVO_3$) in $NaNO_3$ solution (0.01 $mol \cdot L^{-1}$) as background electrolyte. Immediately after adsorption, the clay minerals were separated by centrifugation at 4800 rpm for 10 min.

The adsorption-kinetics experiments were conducted at different time intervals (1 min, 3 min, 5 min, 10 min, 20 min, 40 min, 1 h, 1.5 h, 2 h, 4 h, 6 h and 12 h) with an initial V(V) concentration of 10 $mg \cdot L^{-1}$. The adsorption-isotherms experiments were performed with different initial V(V) concentrations of 1, 2, 5, 10, 15, and 20 $mg \cdot L^{-1}$ at different temperatures (288, 298 and 308 K). The experiments examining the effects of pH on V(V) adsorption capacity were conducted by adjusting the solution pH to 2, 4, 6, 8, 10 and 12 by dropwise addition of $HNO_3$/NaOH with the initial V(V) concentration of 10 $mg \cdot L^{-1}$. The effect of ionic strength was examined in three $NaNO_3$ concentrations (0.001, 0.01 and 0.1 $mol \cdot L^{-1}$) as a background electrolyte. All samples were studied in duplicates.

### 2.3. Analytical methods

The V(V) concentration in the filtrate was determined using an inductively coupled plasma emission spectrometer (ICP-AES, Thermo Electron Corporation, USA). The surface areas of kaolinite and montmorillonite were measured by multipoint Brunauer-Emmett-Teller (BET) analysis (V-Sorb 2800P analyser, Gold APP Instruments Corporation, China). Samples were degassed (heating under vacuum) at 200 °C for 3 h prior to BET measurement. The pH value of reaction solutions was determined by a digital pH meter.

The zeta potentials of kaolinite and montmorillonite were measured using an electrophoresis light-scattering spectrophotometer (Zetasizer Nano, Malvern, Worcestershire, UK). For the zeta potential measurements, 0.2 g clay was added to the beakers containing 50 mL 0.01 $mol \cdot L^{-1}$ $NaNO_3$ at different pH. The dispersions were then dispersed in an ultrasonic bath for 5 min prior to filtration. The dispersions were then quickly poured into a capillary cell to measure the zeta potentials of the precipitates.

### 2.4. Statistical analysis

Lagergren pseudo first-order kinetic model, pseudo second-order kinetic model and intra-particle diffusion model were used to test the dynamic experimental data.

Lagergren pseudo first-order kinetics (Largergren, 1898): $ln\,(Q_e - Q_t) = ln\,Q_e - k_1 t$.

Pseudo second-order model (Blanchard et al., 1984): $\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$

Intra-particle diffusion model (Weber and Morris, 1963): $Q_t = \alpha + kt^{\frac{1}{2}}$

Two typical isotherm models of Langmuir and Freundlich are employed to describe the equilibrium data:

Langmuir model (Langmuir, 1918): $\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$

Freundlich model (Freundlich, 1906): $lg\,Q_e = lg\,K_F + nlgC_e$

The amount of V(V) adsorbed per gram of clay minerals was calculated using the following equation: $Q_e = \frac{(C_0 - C_e)V}{m}$

where $Q_e$ and $Q_t$ are the amounts of V(V) ($mg \cdot g^{-1}$) adsorbed at equilibrium and at time $t$ (min), and $Q_m$ is the maximum adsorption capacity ($mg \cdot g^{-1}$). $C_0$ and $C_e$ are the initial and the equilibrium V(V) concentrations ($mg \cdot L^{-1}$). $k_1$, $k_2$ and $k$ are equilibrium rate constants, and $K_L$, $K_F$, and $n$ are the equation constants. $\alpha$ is the intercept of the linear plot. $V$ is the volume of solution (L), and $m$ is the dry weight of added clay minerals (g). The agreement between experimental data and the models are expressed by the correlation coefficients ($R^2$). A relatively high $R^2$ value indicated that the model successfully follows the kinetics of V(V) adsorption.

Isothermal and kinetics modelling of data was performed using Origin 9.0 and Microsoft Excel 2010. The speciation of V(V) as a function of pH with $[V]_{total} = 10\ mg \cdot L^{-1}$ in 0.01 $mol \cdot L^{-1}$ $NaNO_3$ was calculated by using Visual MINEQL ver. 3.1.

## 3. Results and discussion

### 3.1. Adsorption kinetics

The adsorption kinetics data and fitting models of V(V) adsorption on kaolinite and montmorillonite are shown in Fig. 1. In general, the adsorption process of V(V) on kaolinite exhibited a fast initial rate in the early stage (30 min), followed by a much slower adsorption phase and finally reached equilibrium within 240 min. Montmorillonite showed a more rapid adsorption within 5 min then slowed down and finally reached equilibrium after 360 min. The rapid adsorption process